AD-A061 016 FLORIDA TECHNOLOGICAL UNIV ORLANDO DEPT OF CHEMISTRY F/G 11/10

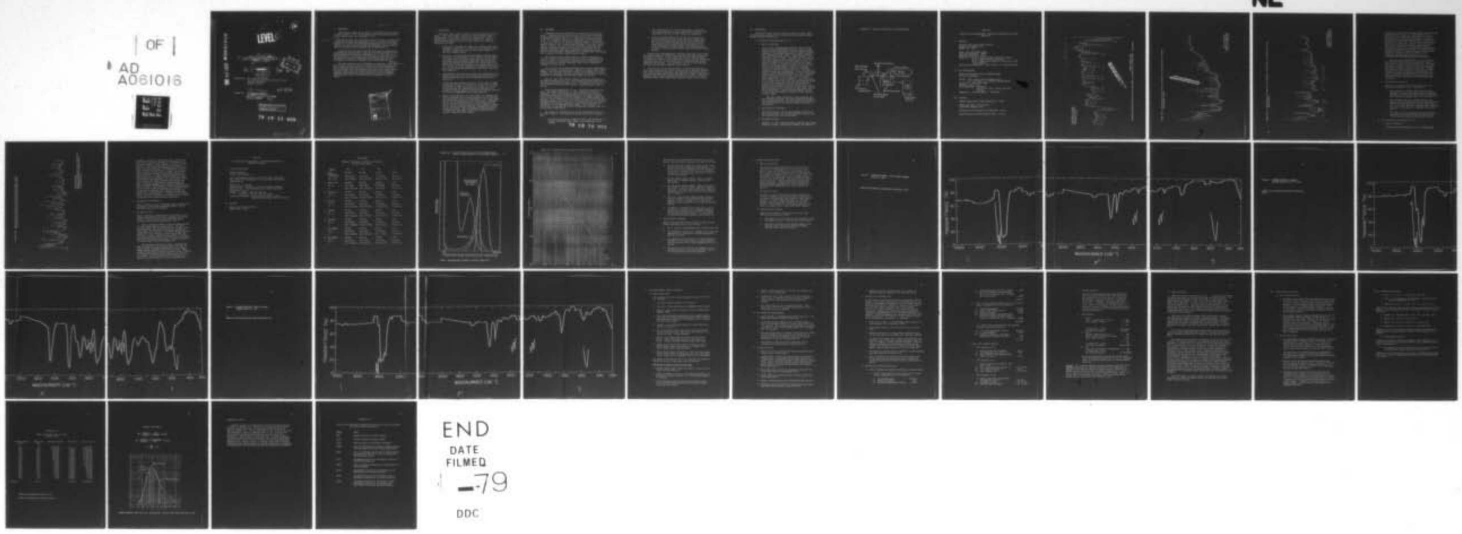
RUBBER IDENTIFICATION PROJECT. PART I.(U)

AUG 78 W W MCGEE N00014-77-C-0621

UNCLASSIFIED NL

| OF |

AD
A061016



END
DATE
FILMED
-79
DDC

coll 8275
NRL

12
B.S.

LEVEL II

6 9 First Year Progress Report.

Rubber Identification Project, Part I.

15 (N00014-77-C-0621) New

11 14 Aug[redacted]78

12 42p.

Prepared for: Drs. Timme and Thompson
Navy Research Laboratory's Underwater Sound
Reference Detachment
Orlando, Florida

410 933

10 Prepared by: Dr. William W. McGee
Department of Chemistry
Florida Technological University
Orlando, Florida
New

410933 mt

I. OBJECTIVES

This research program was designed as a 12-month project scheduled to start on July 1, 1977. Due to delays in the receipt of funds, the project did not start until September 7, 1977.

In general terms, the major goal of the project was to evaluate the techniques of infrared spectrophotometry (I.R.), pyrolysis gas chromatography (P.G.C.) and gel permeation chromatography (G.P.C.) for potential use in a quality control program for monitoring the major constituents of finished rubber components used in Sonar devices.

During the course of the project the major goal was redefined and a more specific one undertaken. Work in the research program was then directed toward evaluating the techniques of I.R., P.G.C. and G.P.C. for potential use in a quality control program for monitoring the polymer fraction of uncured, compounded butyl (isobutylene), Neoprene (chloroprene), and natural (isoprene) based rubber materials.

Once the evaluation of the techniques was completed, it was hoped that a single integrated procedure capable of characterizing the polymer fraction and using aspects of each technique could be designed. Such a procedure would then become a part of a quality control program by which the Naval Research Laboratory Underwater Sound Detachment (NRL/USD) could monitor the polymer fraction of uncured, compounded rubber materials used in the manufacture of components for Sonar devices.

II. CONCLUSIONS

One set of rubber samples was used in all tests described in this report. This set of samples included one uncured sample of each of the following: Butyl #70821, Butyl B-252, Natural Black #35007, Unknown Sample, Neoprene W, and Neoprene #35003 rubber. Based on a laboratory evaluation of this set of rubber samples, the following conclusions were made:

1. Using P.G.C. with optimized sample size, pyrolysis and chromatographic conditions, it is possible to distinguish between the butyl, natural, and Neoprene based rubber samples in the set of samples tested.

2. Using G.P.C. with optimized chromatographic conditions and a previously calibrated bank of G.P.C. columns, the peak molecular weight (Mp), the weight average molecular weight ($\overline{Mw}$), the number average molecular weight ($\overline{Mn}$), and the molecular weight distribution (D:polydispersivity) factors can be calculated for the polymer fraction in each rubber sample in the set. Actual use of these parameters to characterize the polymer fraction should be postponed until additional tests have been completed.

3. Representative thin film I.R. spectra can be obtained for the polymer fraction in each rubber sample once the polymer fraction has been separated from the compounded rubber sample using G.P.C.

4. Collectively the techniques of P.G.C., G.P.C. and I.R. demonstrated the potential to identify and characterize the polymer fraction in each rubber sample in the set. As a result of this finding, the techniques can be integrated into a tentative procedure capable of monitoring the polymer fraction in 4-8 uncured compounded rubber samples per day.

5. Based on the findings in this study, both I.R. (spectra) and G.P.C. (pyrograms) can be used to qualitatively characterize the polymer fraction in the rubber sample. For a given sample, the use of both techniques may not be necessary. Therefore, P.G.C. could be omitted from the integrated procedure and used as a back-up procedure when it is not possible to obtain an I.R. spectrum or where additional information concerning a sample is needed. (This recommendation pertains only to the qualitative characterization of the polymer fraction in uncured, compounded rubber samples.)

III. BACKGROUND

Components made from rubber form an integral part of any Sonar device. Depending upon the component and its use, several different types of rubber may be present in a single Sonar device. Each type of uncured, compounded rubber may be supplied by a different manufacturer. It is possible that several manufacturers may be contracted to supply the same type of uncured, compounded rubber. To assure optimum performance of each finished rubber component in the Sonar device, there is a need by the Naval Research Laboratory's Underwater Sound Reference Detachment (NRL/USD) to be able to analyze each type of uncured, compounded rubber used to manufacture components in Sonar devices for its principle constituents and to monitor these constituents over a period of time in a quality control effort.

The research program conducted by the Chemistry Department at Florida Technological University represents a plan to provide NRL/USD with the capacity of identifying, characterizing, and monitoring the polymer fraction of uncured, compounded rubber used to manufacture components in Sonar devices.

The first step in the research program was to secure representative samples of uncured, compounded butyl, Neoprene and natural based rubber samples. Once received, the rubber samples were subjected to a series of laboratory experiments designed to establish the chemical or physical properties of the polymers in the rubber samples in the set.

The next step in the research program involved the evaluation of infrared spectrophotometry (I.R.), gel permeation chromatography (G.P.C.), and pyrolysis gas chromatography (P.G.C.) for potential use in monitoring the polymer fraction in each uncured, compounded rubber sample in the set.

Infrared spectrophotometry is a well established analytical technique. The rubber industry has used this technique for years to characterize new or experimental polymeric materials and to monitor the polymer composition of compounded rubber. The spectral characteristics of most polymers used in the manufacture of rubber products are available in the literature or can be readily produced in the laboratory. The major problem in the analysis of the polymer fraction in an uncured, compounded rubber sample is separating of the polymer from the other constituents in the compounded rubber sample. Once separated, a satisfactory IR spectrum can usually be obtained by casting a thin film of the polymer from solution.

Gel permeation chromatography has become a workhorse technique in the rubber industry. The reasons for the interest in this techinque are:

1. The polymer and additive components used in the manufacture of uncured, compounded rubber sample can be separated, and recovered.

2. Once separated from the uncured rubber sample, the polymer (and other components) can be characterized by infrared spectrophotometry (as well as other analytical techniques).

3. Using a calibrated bank of GPC columns, it is possible to calculate several molecular weight related parameters which may be used to characterize the polymer under examination. The calibrated bank of columns may also be used to detect normal and abnormal molecular weight distributions in the polymer fraction in a rubber sample. This information may be useful in predicting wear characteristics of finished rubber samples.

Pyrolysis gas chromatography is currently being used in the rubber and polymer industries in pilot plant and production line applications to monitor the quality of both uncured and finished rubber products. The destructive nature of this technique can provide valuable information concerning the nature of the polymer used to manufacture the uncured compounded rubber sample. This information may not be available from the other two techniques evaluated in this project.

The final step in the research project involved the integration of the most useful aspects of each of the analytical technique described into a single analysis procedure. The information obtained from this integrated procedure should provide NRL/USRD with a means of identifying, characterizing, and then monitoring the polymer fractions in uncured, compounded rubber used to manufacture components used in Sonar devices.

IV. EXPERIMENTAL

A discusison of the procedure used to prepare the rubber sample for instrumental analysis will be presented in the integrated rubber analysis procedure (Section V).

A. Pyrolysis Gas Chromatography (P.G.C.)

1. Basis of Operation:

Pyrolysis gas chromatography represents the successful coupling of two established procedures; pyrolytic degradation and gas chromatography, into one viable analytical technique. The pyrolyzer consists of a pyrolysis probe and a regulated voltage supply. Diagram One contains a schematic of the pyrolyzer. The probe contains a silica tube around which is wound a platinum wire. The probe is electically connected to the power supply and fits, by means of a knured screw and gas tight seal, in a small heated oven which is connected directly to the injection port of a gas chromatograph. To pyrolyze a sample, a weighed or accurately measured portion of the sample is placed in the silica tube in the probe. The probe is connected to the gas chromatograph. Current from the power supply is passed through the platinum wire for a specific period of time causing the probe to heat to a predetermined temperature. At this temperature, the sample should degrade into volatile components which are carried by the helium carrier gas to the gas chromatography column. As the volatile components move down the column, they separate into fractions of similar chemical nature. A hydrogen flame detector at the end of each column, detects these separated volatile fractions as they emerge from the end of the column. A small dedicated computer is used to record the chromatographic variation of the amplified detector signal.

Once the variable parameters in this procedure have been optimized, pyrolysis of a sample should be reproducible and hopefully produce volatile fragments which can be used to characterize the orginal molecule (the polymer in this project).

2. Optimization of Parameters:

Table One contains a list of the equipment used in this part of the project, the variable parameters studied, and the optimized value for each parameter.

3. Discussion of Data:

Figures 1, 2, and 3 contain pyrograms (pyrolysis gas chromatograms) for butyl (isobutylene), Neoprene (chloroprene)

DIAGRAM ONE - Schematic of Pyrolysis Gas Chromatograph

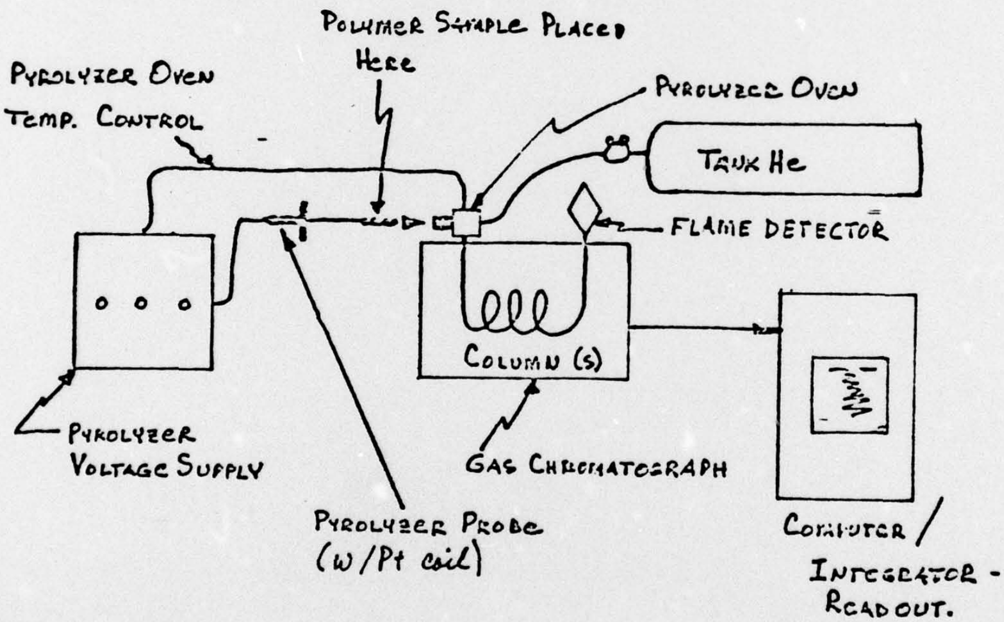


TABLE ONE

Pyrolysis Gas Chromatography: Equipment Used/Optimized Variable Parameters

I. Pyrolyzer

CDS Model 100 Series Solids Pyrolyzer
Chemical Data Systems, Inc.
Oxford, Pa. 19363

Probe: Coil with Quartz Liner
Pyrolysis Temperature: 1000°C
Duration of Pyrolysis: 2 sec.
Sample Size: 50 μg of solid, uncured, compounded rubber or
50 μg of separated polymer fraction.
(Note: samples were weighed on a Cahn Model #4700 Electrobalance)
Pyrolyzer Oven Temperature: 250°C (same as G.C. injection port).

II. Gas Chromatograph

Hewlett Packard Model #5711 Gas Chromatograph
Palo Alto, California

Columns: Glass-(Glass system throughout)-Dual
6' x 1/4"; OV-1; 3% on Chromo W/AW/DMCS/80/100
Carrier/Flow: Helium/30 cc/min
Detectors: Dual F.I.D.
Oven Temperature: Programmed:
35°C (2 min. hold) → 200°C(2 min hold)
@8°C/min.
Temperature , Injector/Detector: 250°C/300°C

III. Recorder

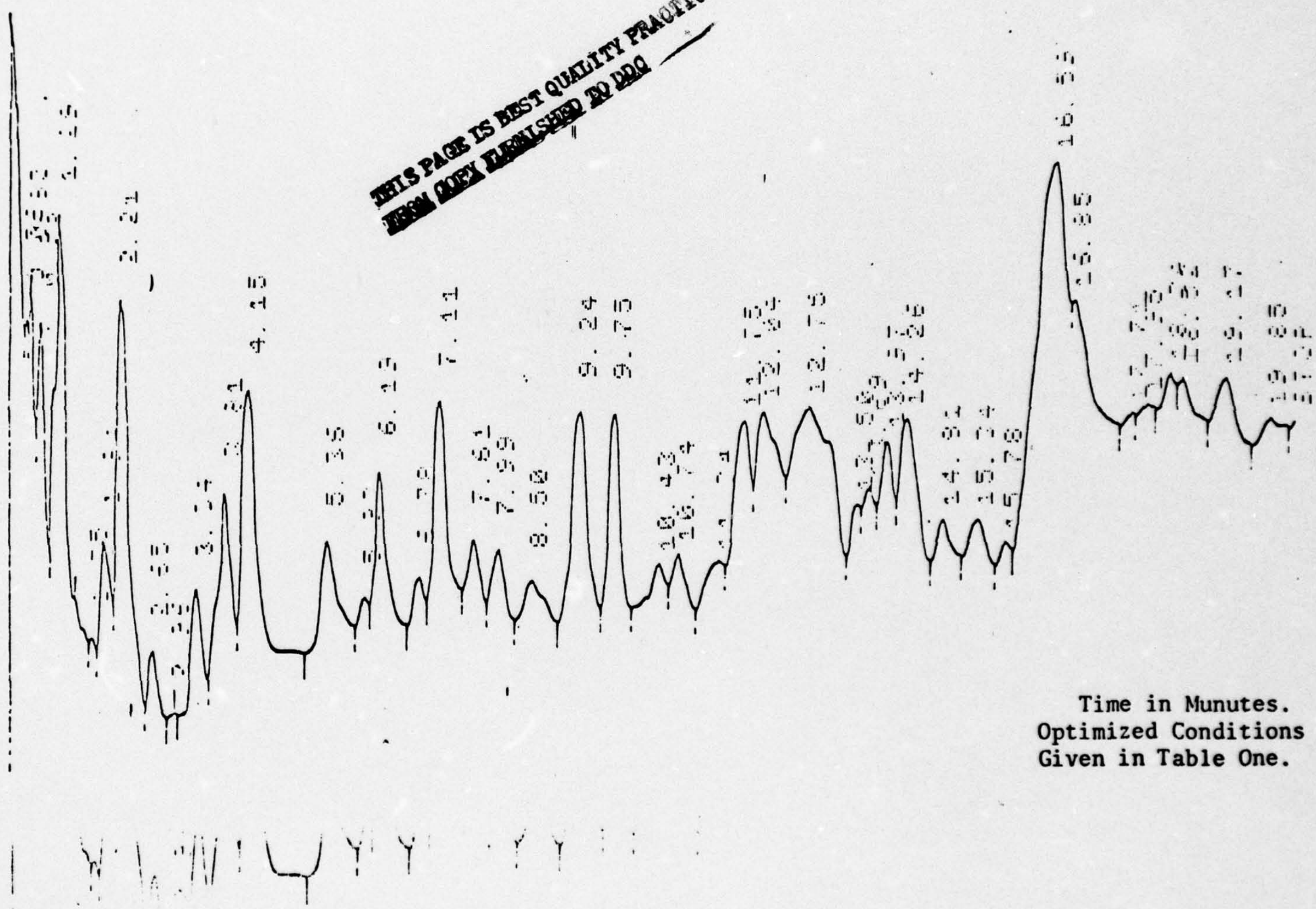
Hewlett Packard Model #3380A Reporting Integrator

Linear Time Scale: 0.01 minutes
Logarithmic Response scale

Average Time of Pyrolysis Gas Chromatogram: 30 min.

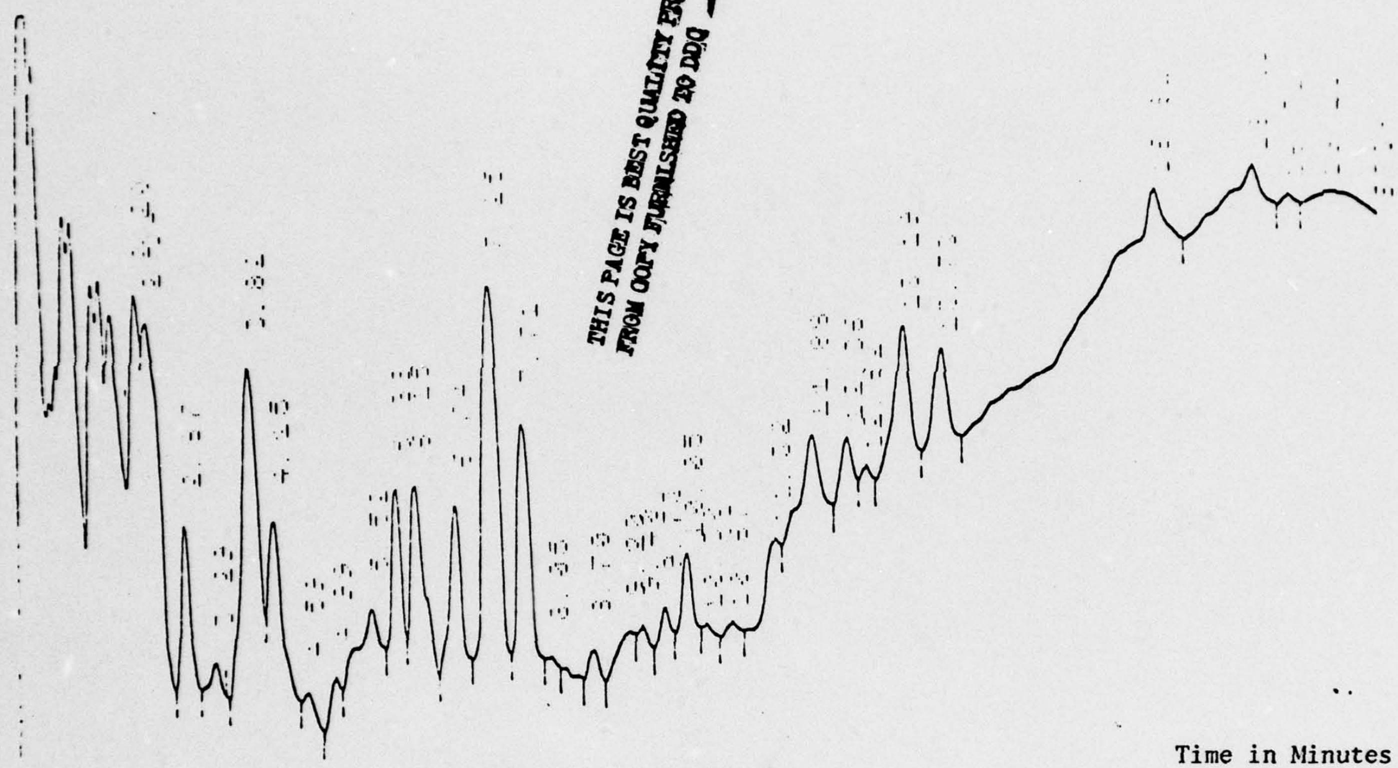
Normal Variation in Peak Retention Time ± .05 min.

Figure One Representative Pyrogram for Compounded, Uncured and Chloroprene (Neoprene) Based Rubber Sample



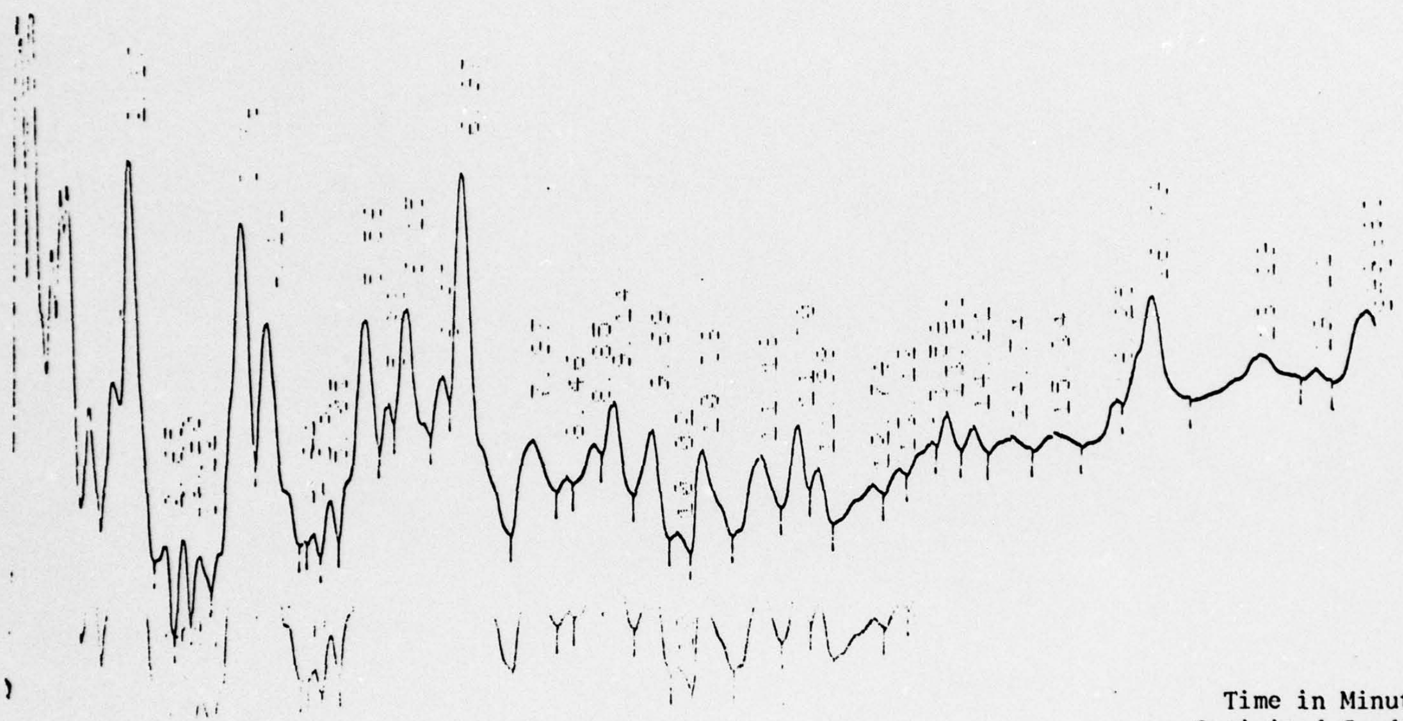
Time in Munutes.
Optimized Conditions
Given in Table One.

Figure Two - Representative Pyrogram for Compounded, Uncured Natural (Isoprene) Based Rubber Sample



Time in Minutes
Optimized Conditions
Given in Table One.

Figure Three - Representative Pyrogram for Compounded, Uncured Butyl (Isobutylene) Based Rubber Sample



Time in Minutes
Optimized Conditions
Given in Table One.

and natural (isoprene) based rubber samples generated using conditions given in Table 1. Identification of the polymer type in a compounded rubber sample is based on the sequencing peaks, by time of elution, as they are recorded by the recording integration or by overlaying pyrograms on a light box. For the samples studied, each basic polymer type (butyl, Neoprene, and natural) was found to have distinctive patterns of peak elution. A majority of the peaks in each pyrogram originate from the polymer fraction of the sample. This observation is illustrated in Figure 4 which contains a pyrogram of the separated Neoprene (chloroprene) polymer. (For comparison purposes refer to Figure 1; which is a pyrogram of compounded Neoprene rubber sample).

When making an identification, it is the reproducibility of the retention time and sequencing of peaks which should be noted and not the peak size. Some minor variations in retention time result from operator error and minor variances in instrument operation. Normally, such errors are unidirectional and are nearly constant throughout the entire pyrogram. With experience, the analyst soon learns to recognize and distinguish differences in retnetion time originating from polymer composition from these originating in instrument/operator variability.

4. Limitations of Technique:

Based on the laboratory results from this study, the following limitations of P.G.C. were noted:

a. P.G.C. requires a moderate amount of time (30-45 min/sample) and some moderately expensive equipment ($19,000) to produce data which may be available from other techniques evaluated (e.g., I.R. and G.P.C.).

b. Basic polymer types (e.g., butyl, Neoprene, and natural) can be differtiated; however, differentiation between different members of the same polymer type (e.g., butyl from chlorbutyl, Neoprene from Neoprene W). could not be made using the conditions indicated in Table 1.

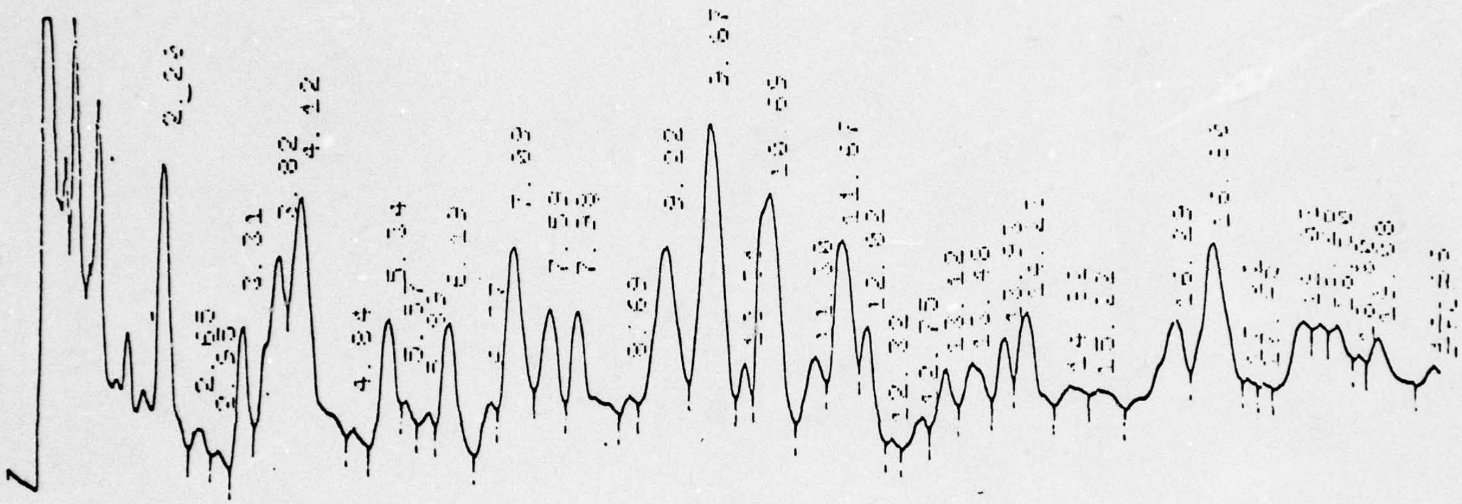
c. The extent of pyrolysis could not be quantitatively reproduced using the conditions indicated in Table 1 (or any other conditions tried in this study).

B. Gel Permeation Chromatography (G.P.C.)

1. Basics of Operation:

Gel permeation chromatography is not a chromatographic

Figure Four - Representative Pyrogram for Chloroprene (Neoprene) Polymer Fraction Separated from Compounded Neoprene Rubber Stock



Time in Minutes
Optimized Conditions Given in Table One.
(Compounded Neoprene Pyrogram shown in Figure One.)

separation technique in the normal sense of the term but a "size-exclusion" technique in which molecules are separated by their size in solution. A series or "bank" of G.P.C. columns containing porous polymer beads of known pore size effects the separation of the molecules. When a solution of molecules of different size (in solution) is passed down the bank of columns, the molecules either penetrate the pores of the polymer beads or go around the beads. It requires more residence time for the molecules to go through the beads than around them, thus producing the separation. For this process to function properly, very dilute solutions of molecules are used. A variety of detectors and readout devices are used to note the emergence of the molecules from the bank of columns. Using polymers of known molecular weight/size, the elution time of molecules from the bank of GPC columns can be calibrated thus making it possible to characterize the polymer and to estimate the molecular weight of an unknown molecule. In addition, once separated by the G.P.C. columns, the molecules may be collected and examined using other analytical techniques.

2. Optimization of Parameters:

Table Two contains a list of equipment used in this part of the project, the variable parameters studied, and the optimized value for each parameter.

3. Discussion of Data:

Figure 5 contains a representation of the relative G.P.C. elution characteristics for butyl, Neoprene, and natural polymers in the respective compounded rubber samples using the optimized conditions given in Table 2.

Table 3 contains a summary of the gel permeation data for each polymer studied in this project. The peak molecular weight (Mp) was determined from the peak elution time (volume) of the polymer by using the polystyrene calibration curve (Figure 6). The number average molecular weight ($\bar{M}n$), weight average molecular weight ($\bar{M}w$), and dispersitivity (D: a measure of the breadth of a molecular weight distribution) were calculated for each polymer from the corresponding chromatogram. A sample calculation for typical data is given in Appendix One.

With respect of the data in Table 3 an attempt was made to survey existing literature sources for data of similar nature for comparison purposes. The literature search was not successful in locating such data. Until relevant data becomes available, the data in Table 3 should be viewed and interpreted with respect to the goals of the project. A brief discussion of the potential use of molecular weight parameters is given in Appendix One.

Table Two

Gel Permeation Chromatography: Equipment Used/Optimized Variable Parameters

I. Liquid Chromatograph:

Waters Associates
Milford, Massachusetts

Liquid chromatograph consists of a U6K Injector, Model 6000 Pump, Model 440 UV detector (254 nm), and Model 401 Refractive Index Detector.

Sample Size: 0.25-0.50%
Injection Size: 100-600 μℓ (varies with polymer studied)
Mobile Solvent: Tetrahydrofuran (THF), Burdick and Jackson
Temperature: Room
Columns: μ Styragel; Waters Associates
Pore Size: 10^6, 10^5, 10^4, 10^3, 500Å
Calibration Standards: Narrow Range polystyrene samples
Molecular weight range 2,300 to 2,300,000

II. Recorder

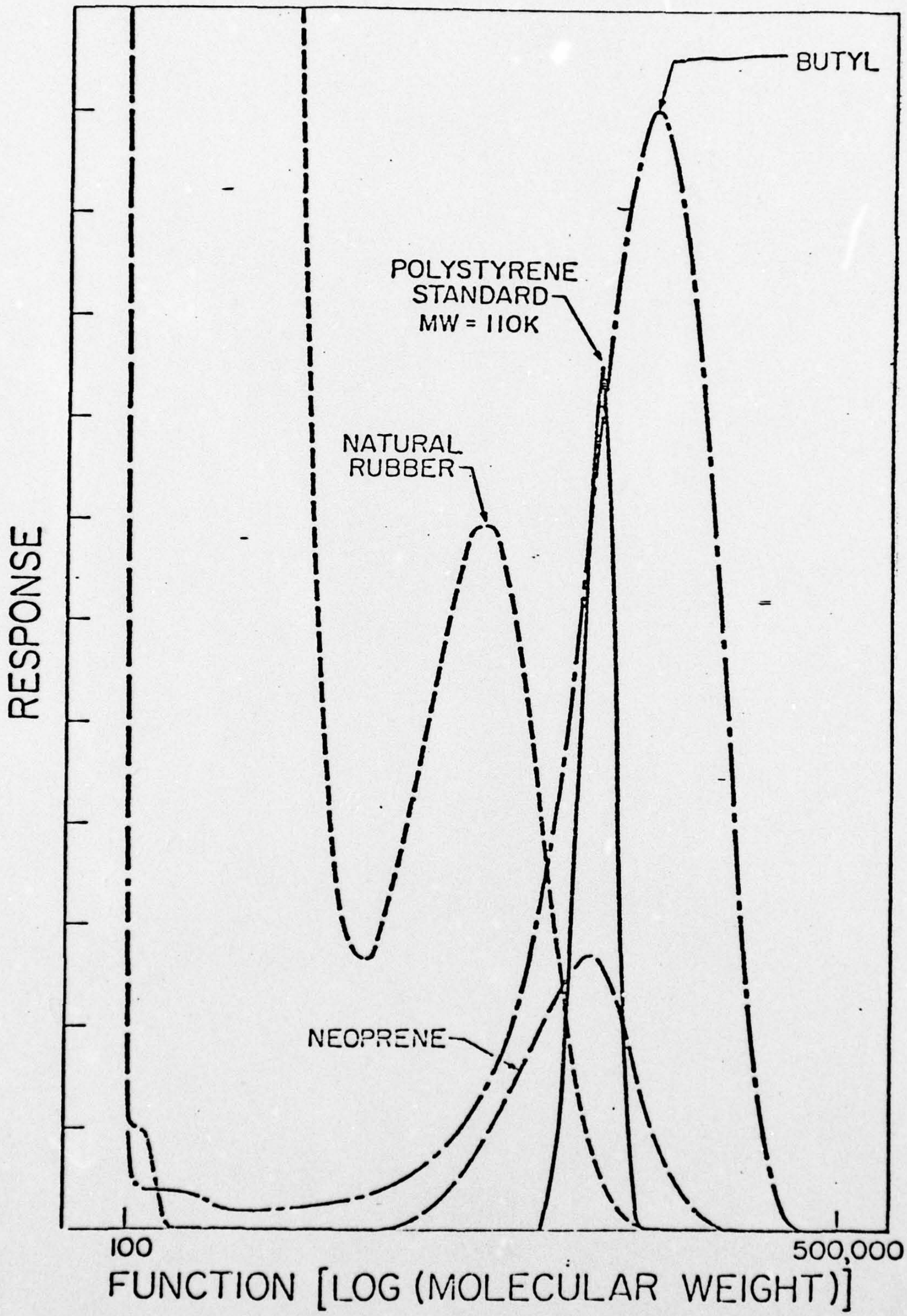
Houston Servo Writer Dual Pen
Chart Speed - 1"/min.

TABLE THREE

Summary of GPC Data: Polymers in Compounded, Uncured Rubber Samples

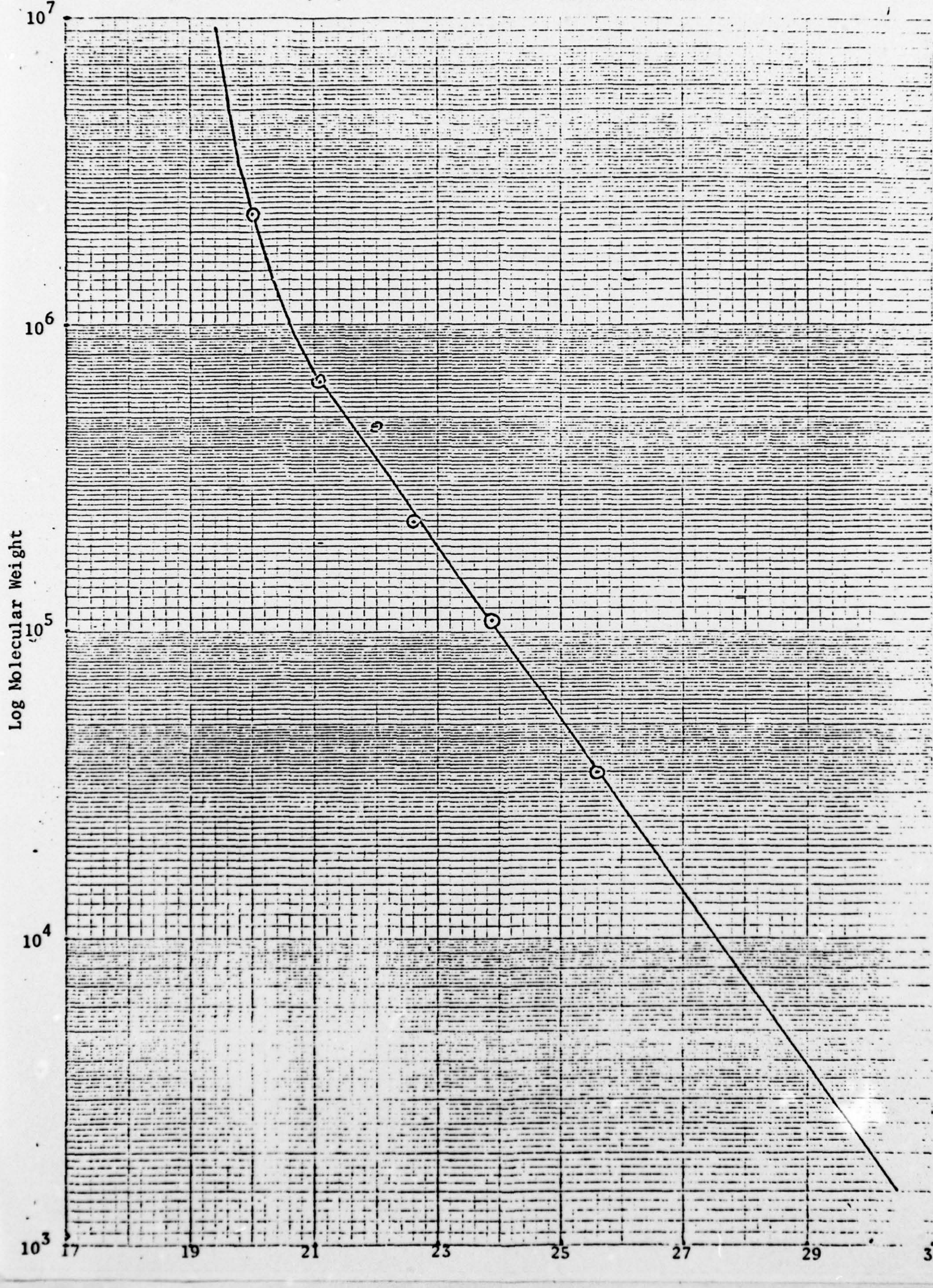
	Sample/	$\overline{M}p$	$\overline{M}w$	$\overline{M}n$	D
1.	Butyl (electrical grade Butyl)	285,000	465,000	118,100	3.98
		(10;20,000)	(4;78,700)	(4;14,900)	(4;0.23)
	(n, σ , R)	(235-400,000)	(361,-544,000)	(96,-127,000)	(3.76-4.30)
2.	Butyl B-252	210,000	359,300	104,000	3.49
	(n; σ)	(16;1,000)	(6;70,700)	(6;13,000)	(6;0.72)
	R	(200,-240,000)	(296,-488,000)	79-117,000	(2.77-4.47)
3.	Neoprene W	130,000	181,100	44,400	4.53
	(n; σ)	(11;14,000)	(5,;38,300)	(5;6,600)	(5;0.46)
	R	(115,-135,000)	(193,-233,000)	(39,-52,700)	(3.89-5.18)
4.	Natural	530,000	777,300	167,500	4.79
	(n; σ)	(13;25,000)	(6;86,700)	(6;37,800)	(6;0.84)
	R	(470,-740,000)	(632,-873,000)	(125,219,000)	(3.48-5.01)
5.	Unknown	180,000	278,600	77,600	3.66
	(N; σ)	(10;11,000)	(5;24,100)	(5;16,100)	(5;0.46)
	R	(160,-200,000)	(262,-314,000)	(58,-102,100)	(3.08-4.36)
6.	Neoprene	120,000	182,400	37,400	4.87
	(N; σ)	(10;10,000)	(5;40,800)	(5;5,500)	(5;0.63)
	R	(100,-148,000)	(128,-242,000)	(28,7-42,800)	(4.26-5.64)
7.	Cerco#C6N5	120,000	156,000	57,200	2.77
	(n; σ)	(6;10,000)	(4;37,100)	(4;17,000)	(4;0.25)
	R	(100,-148,000)	(104,-180,000)	(51,-71,400)	(2.52-3.05)
8.	Cerco#48N5	105,000	160,200	41,000	3.86
	(N; σ)	(8;12,000)	(6;61,100)	(6;13,900)	(6;0.35)
	R	(97,-135,000)	(82,-260,000)	(19,8-61,400)	(3.39-4.23)

Figure Five - Elution Characteristics of Butyl, Neoprene and Natural Polymers Relative to Polystyrene Standard*



*Note: Chromatography conditions listed in Table Two.

Figure Six - Polystyrene Gel Permeation Calibration Curve



While definitive interpretation of the data may be premature, some observations concerning the data can be made.

a. The peak molecular weight and elution volume of the polymer (Mp) can be reproducibly generated (i.e., Mp varies ±10.000-25,000 depending upon the molecular weight and the portion of the log scale on which it is measured. (Elution volume varies ±0.2 ml over a 30 min. chromatogram.)

b. For the rubber samples studied, (Table 3) natural rubber has the highest numerical values for Mp, $\overline{M}w$, and $\overline{M}n$.

c. For the rubber samples studied, (Table 3) Neoprene and Neoprene W have the lowest numberical values for Mp and $\overline{M}n$. The Cerco Samples were said to contain a Neoprene type polymer (data from this study supports this statement).

d. The G.P.C. data for the "Unknown" sample (Table 3) does not resemble the data generated for the other samples in the set; although, it is closest in molecular weight parameters to the butyl based rubber samples.

e. In addition to providing data which may be used to characterize a polymer, G.P.C. provides a means of separating the polymer from the other constituents in the compounded rubber samples. In this project the separated polymer fraction was analyzed by I.R.

4. Limitations of Technique:

Based on the laboratory results from this study, the following limitations of G.P.C. were noted:

a. G.P.C. runs are time consuming (~30-40 minutes per run).

b. The performance of the G.P.C. columns must be routinely monitored (i.e., polystyrene calibration standards must be run daily).

c. All samples to be run on the G.P.C. must be filtered through a 0.45 μm filter prior to chromatographing. This step prevents an accidental plugging of the G.P.C. columns.

d. The absence of G.P.C. data in the literature for the polymers studied in this project prevents a definitive interpretation of the data generated.

C. Infrared Spectrophotometry

1. Basics of Operation:

The polymer fraction separated by G.P.C. was cast as a thin film (by evaporating the solvent-THF) on a AgBr plate. The plate (and thin film) were mounted in a 4x beam condenser and the infrared spectrum of the polymer was scanned and recorded for the 2-40 μ range. Using this technique, satisfactory spectra were obtained using as little as 500 μg of polymer. Depending upon the polymer, one to three G.P.C. runs were required to collect this amount of polymer. A Perkin-Elmer Model 467 Infrared Spectrophotometer equipped with a 4x Beam Condenser and Wilk's #018-4074 AgBr plates were used to obtain the spectra.

2. Discussion of Data:

Figures 7, 8, and 9 contain representative spectra for the butyl, Neoprene, and Natural polymers separated from the respective compounded rubber samples. These spectra (Figure 7, 8, and 9) compare favorably with reference spectra (literature and lab generated) for the same polymer. Classification of the polymer as a butyl, Neoprene, or natural type is direct and straight forward.

3. Limitations of Technique:

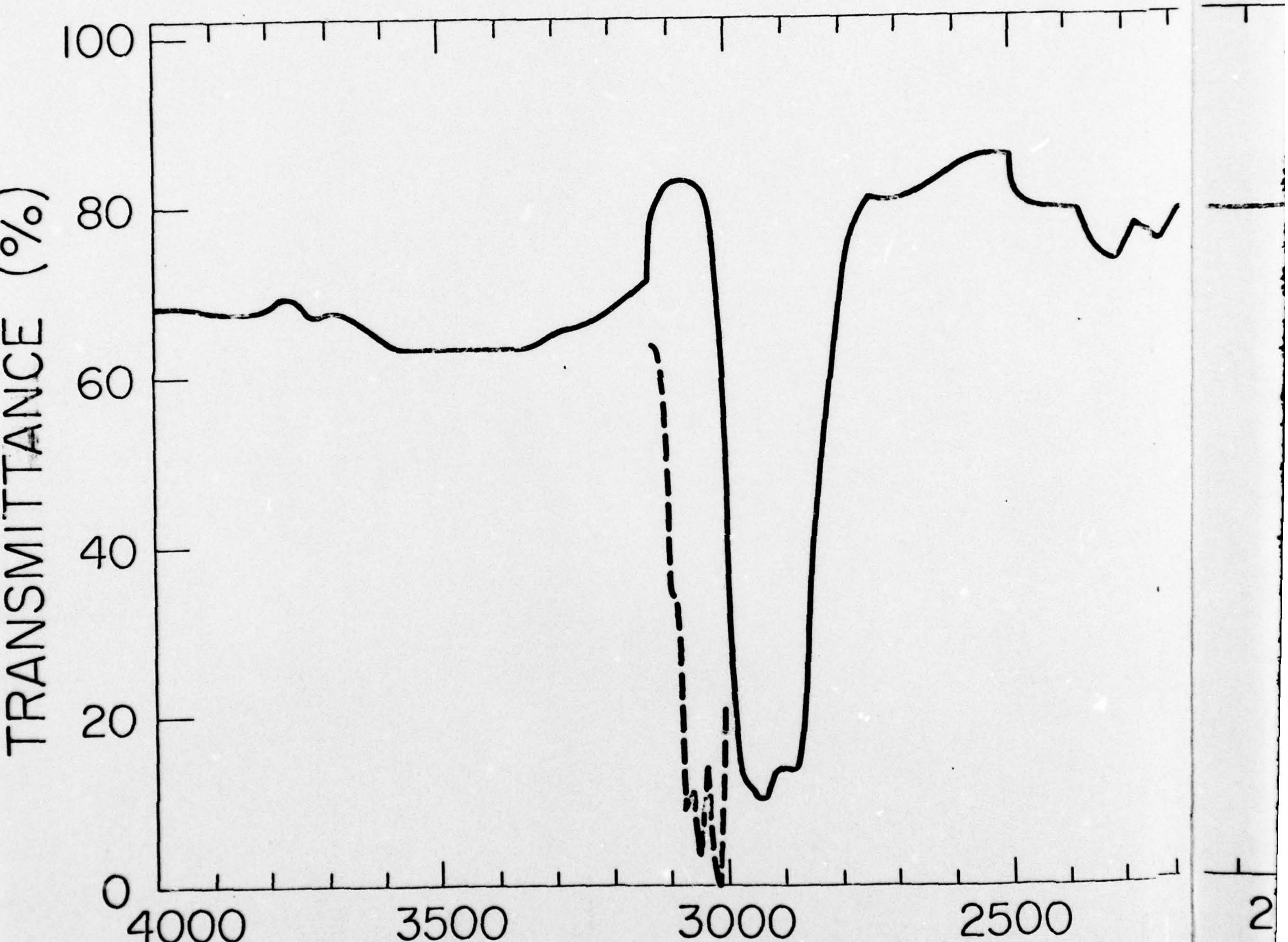
Based on the laboratory results from this study, the following limitations were noted:

a. Variations in the I.R. spectra due to molecular weight (as suggested in the literature) were not detected.

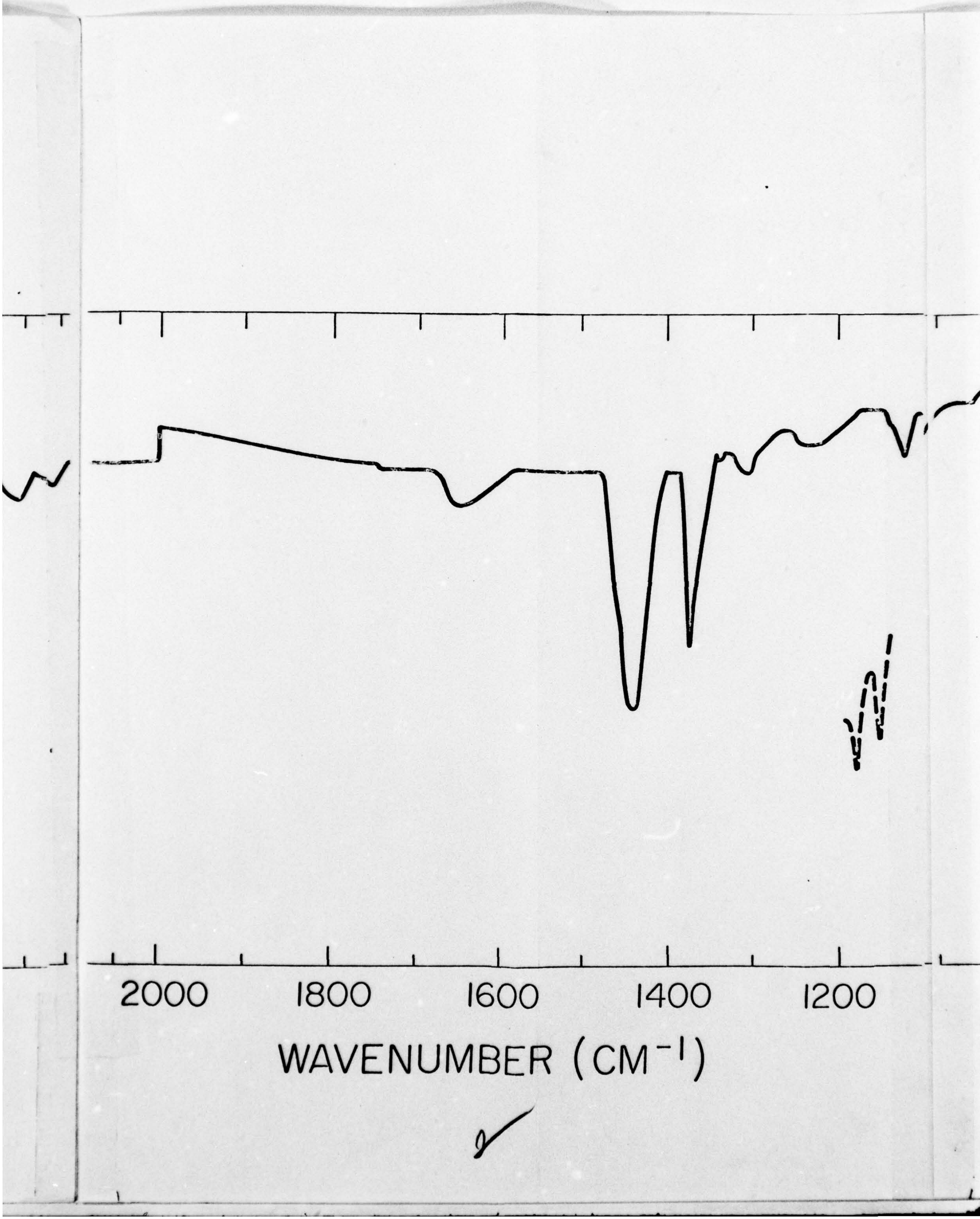
b. Significant variations among polymer samples of the same type (Butyl B252/Butyl 35007 and Neoprene/Neoprene Type W) were not detected.

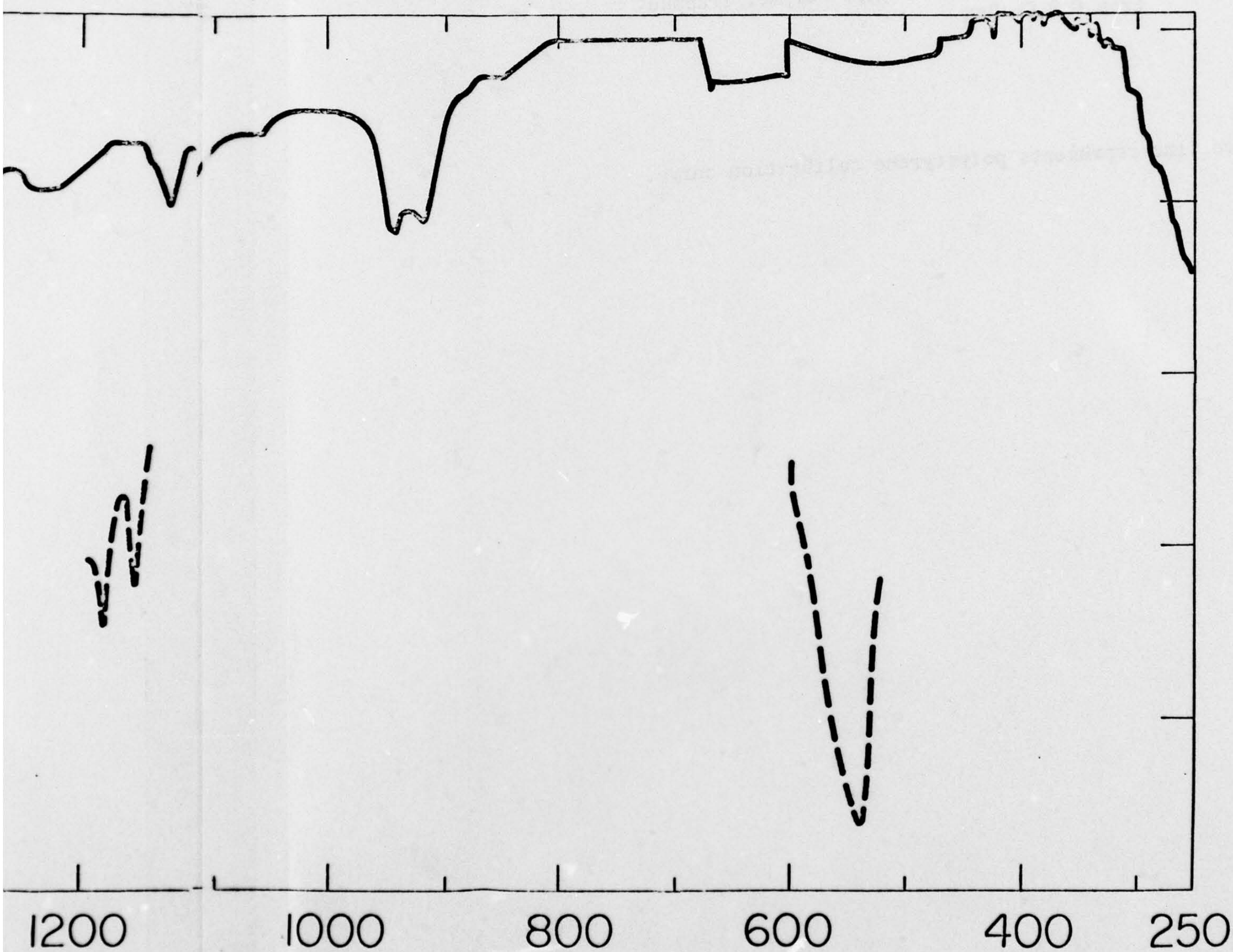
Figure 7. INFRARED SPECTRUM - Butyl Polymer Trapped from G.P.C. Run

Dashed line represents polystyrene calibration curve.



TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
2

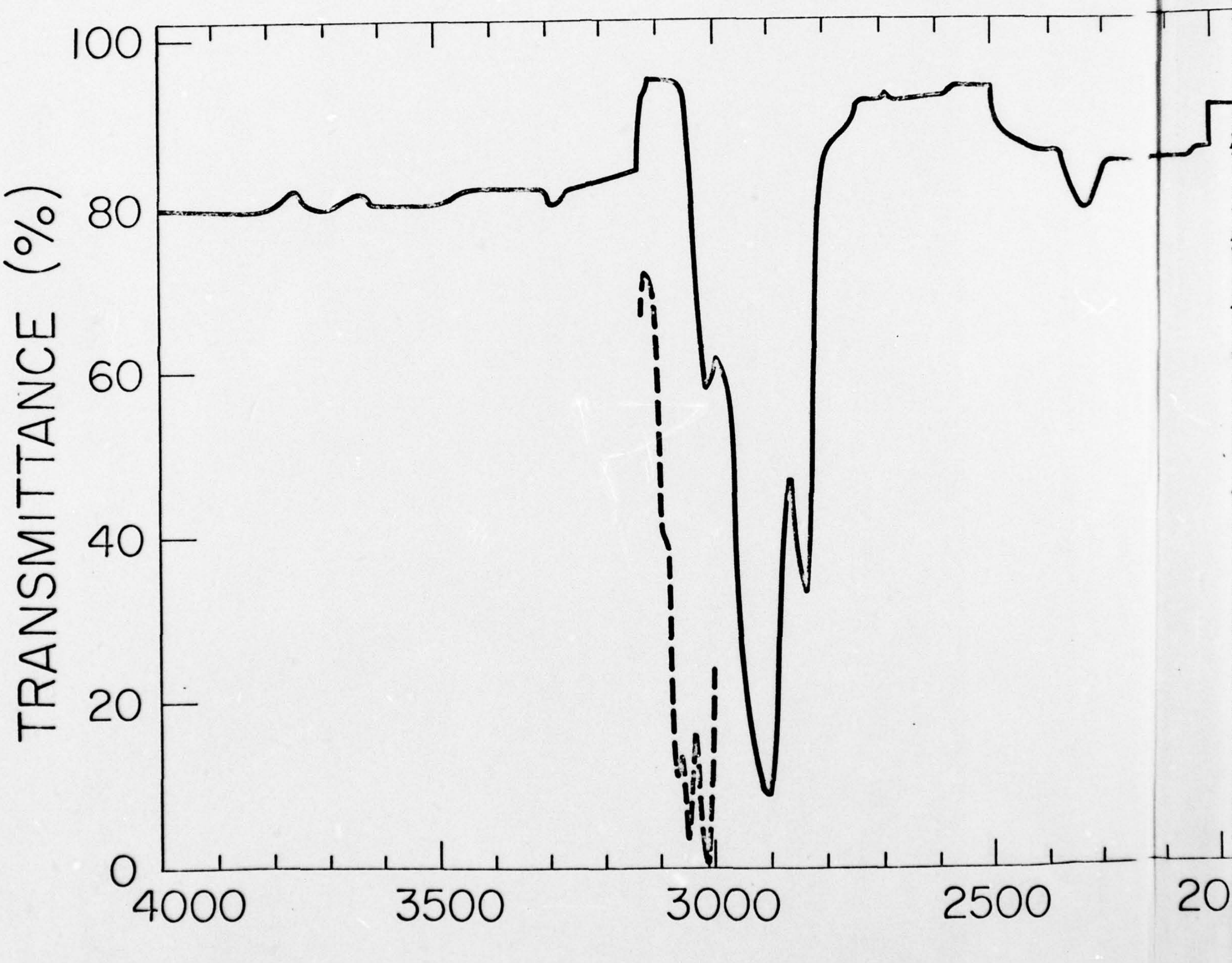

2000
1800
1600
1400
1200
WAVENUMBER (CM^{-1})



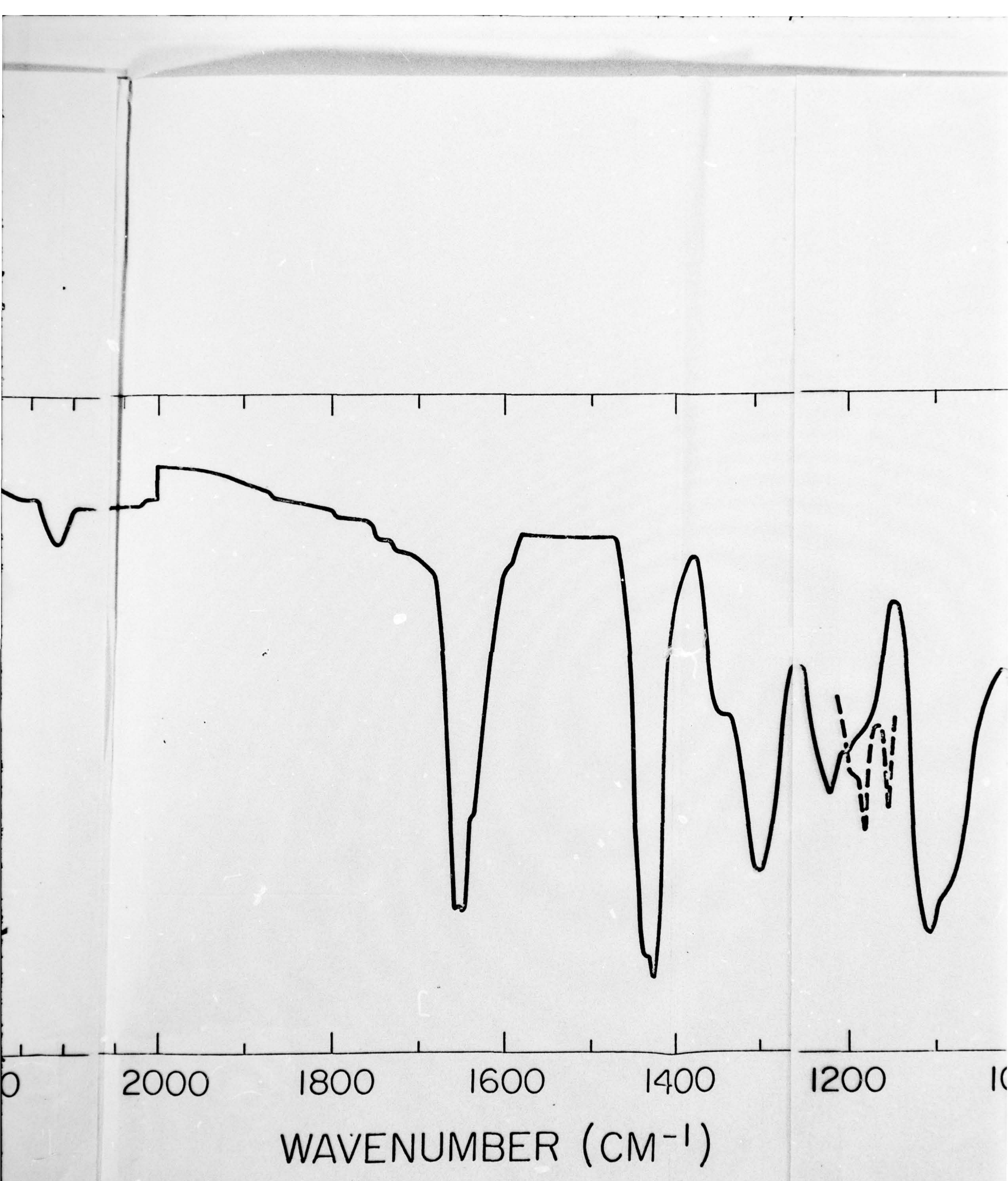
3

Figure 8. INFRARED SPECTRUM - Neoprene
Polymer Trapped from G.P.C. Run

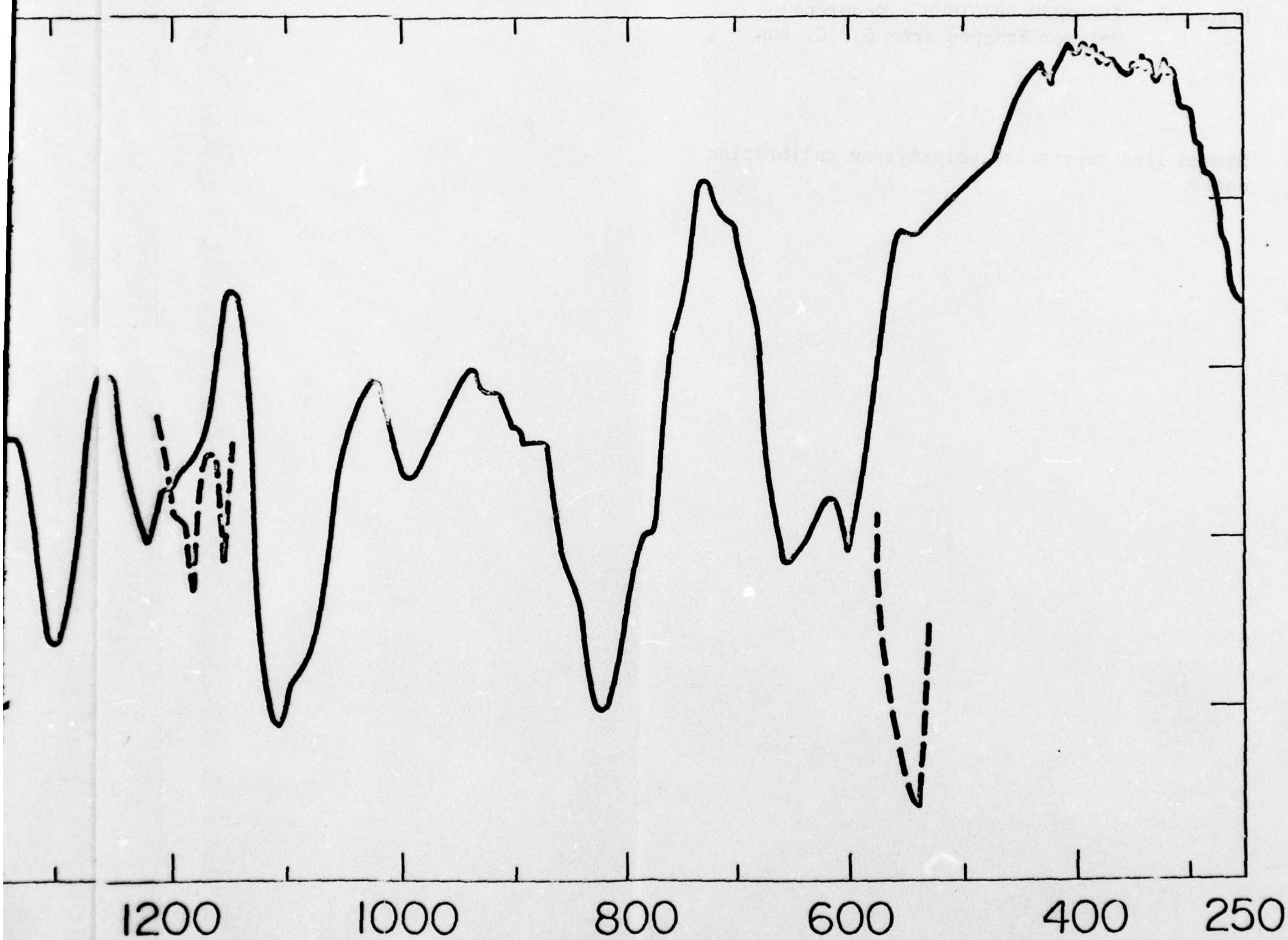
Dashed line represents polystyrene calibration curve.



TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500
20



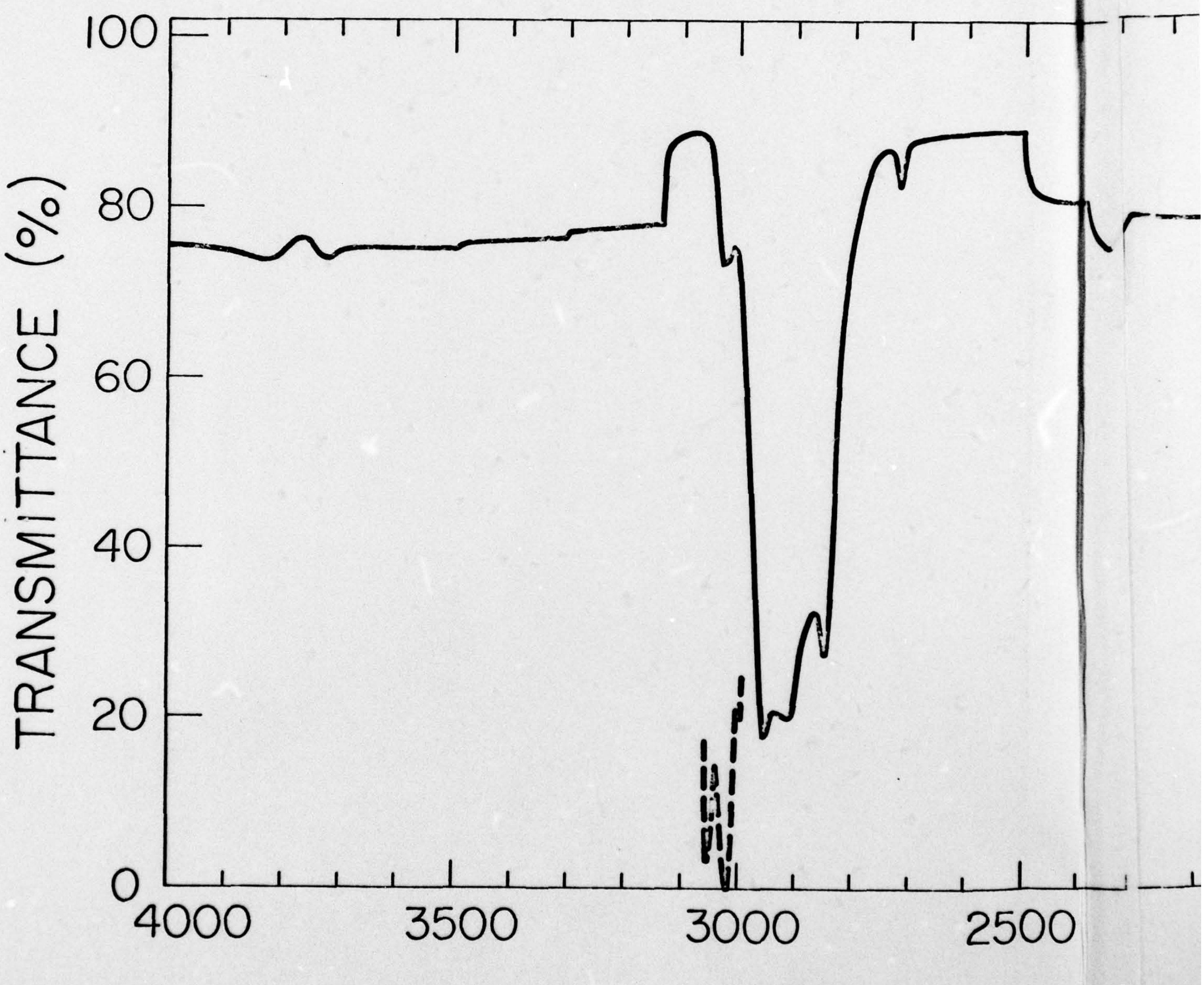
8

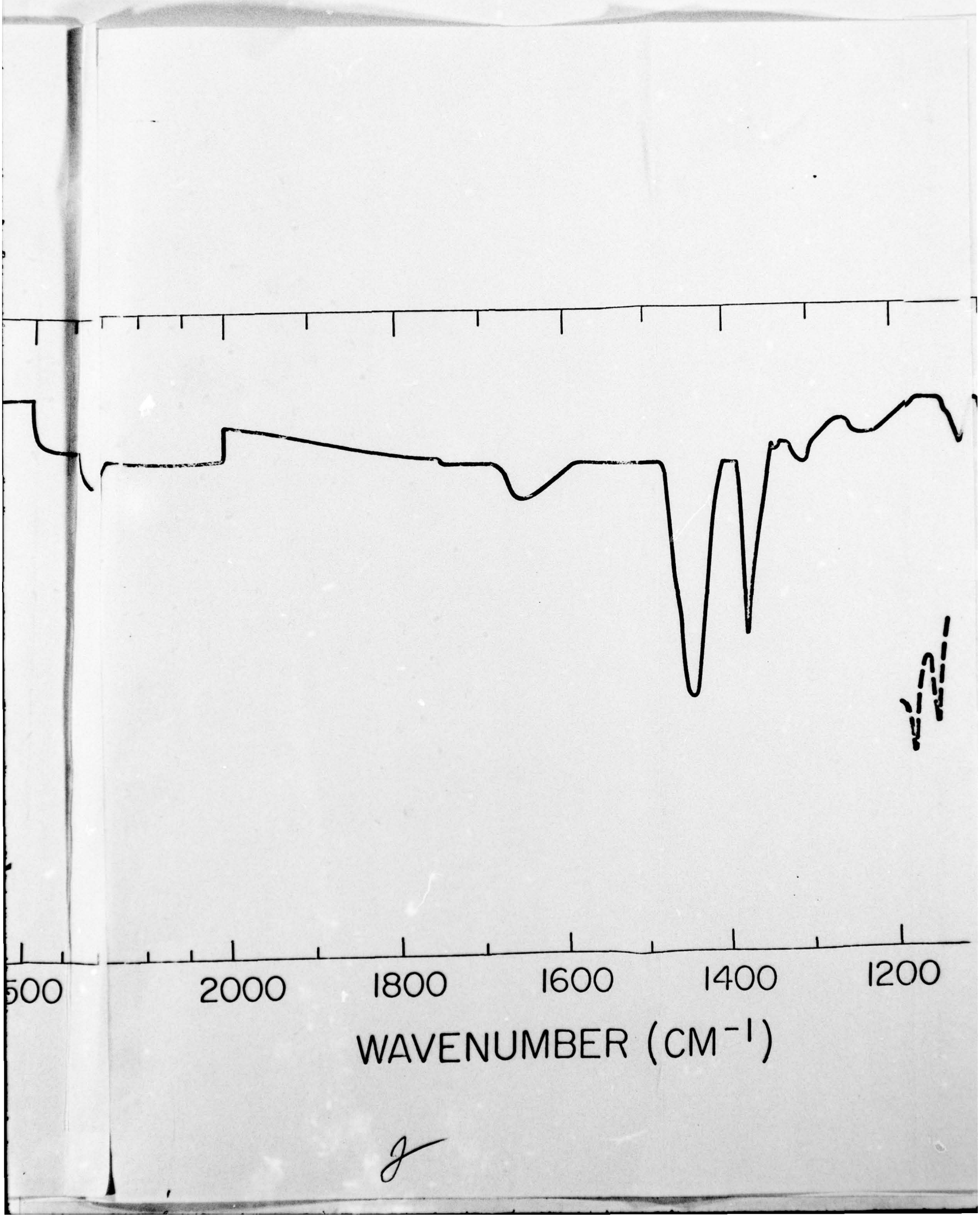


3

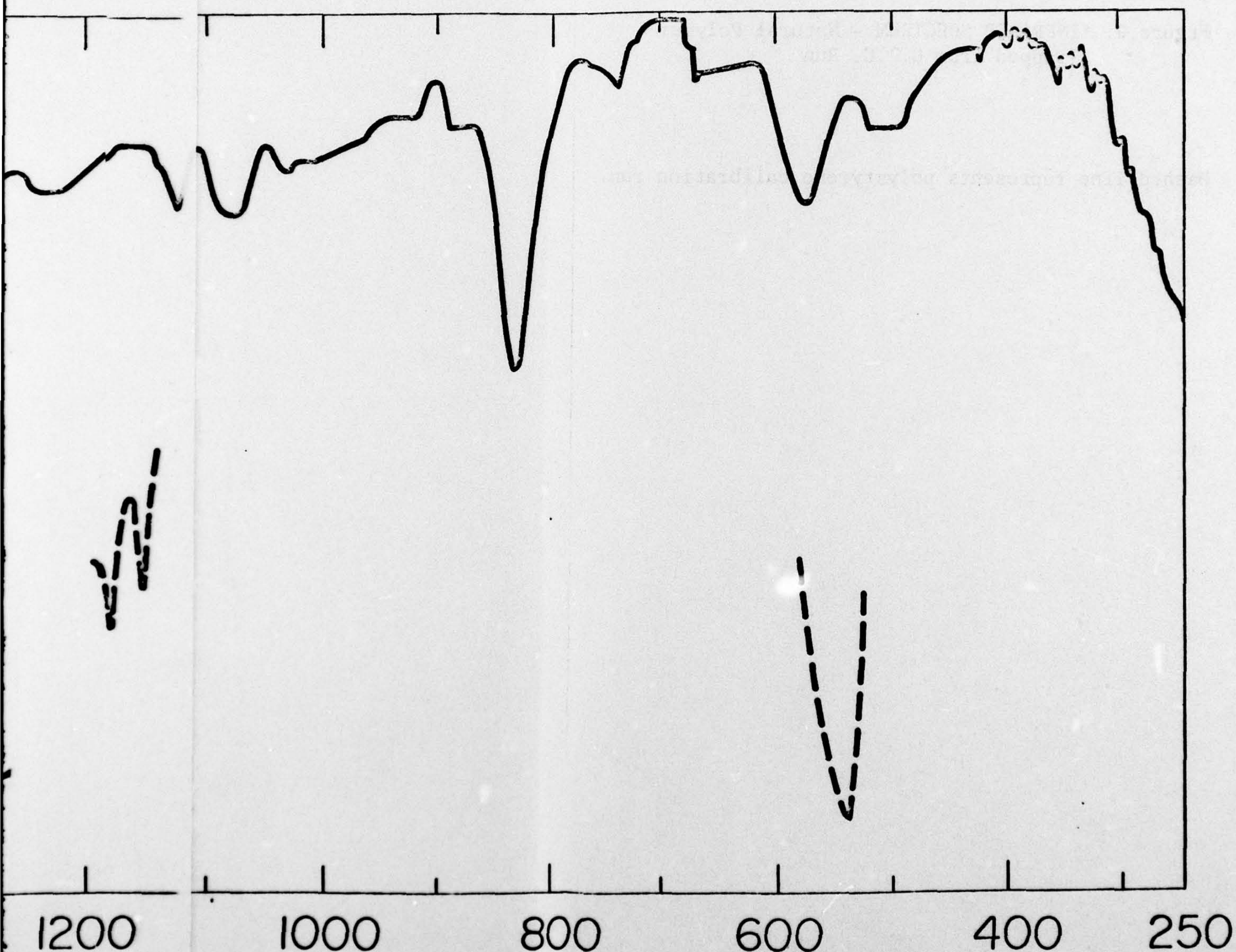
Figure 9. INFRARED SPECTRUM - Natural Polymer
Trapped from G.P.C. Run

Dashed line represents polystyrene calibration run.


TRANSMITTANCE (%)
100
80
60
40
20
0
4000
3500
3000
2500



500
2000
1800
1600
1400
1200
WAVENUMBER (CM^{-1})



3

V. Integrated Rubber Analysis Procedure

A. Sample Preparation

The following steps were used to prepare the sample for G.P.C./I.R. analyses.

1. Cut rubber sample into small (1 mm^2) piece.

2. Weigh out a 250 mg portion of the compounded rubber sample.

3. Bubble N_2, for 1 minute, through 10.0 ml of orthodichlorobenzene (ODCB).

4. Place ODCB and weighed polymer sample in a tightly sealed, screw capped test tube, and gently agitate until dissolved. Depending upon the polymer, 10-60 minutes will be required to dissolve the sample.

5. Prepare a vacuum filtration flask for a ASTM #10-30 fine, fritted glass filter.

6. Fill fritted glass filter (2/3 full) with Celite diatomaceous earth filter aid. Wash Celite with several 2-3 ml portions of ODCB. Discard washings.

7. Quickly filter rubber solution through Celite/fritted filter. Allow the polymer solution to drain from the filter. Collect and remove filtrate from vacuum flask.

8. Quickly filter the filtrate (step #7) through a Waters #26870 Organic Sample Clarification Kit using 0.45 μm Waters #66874 Organic Solvent filter.

9. Collect this filtrate (step #8) in a 10-15 ml screw capped sample bottle; bubble N_2 through the filtrate, and tightly cap the sample bottle (aluminum liner on cap is preferred).

The sample is now ready for G.P.C./I.R. analysis and should be stored out of direct light until ready for analysis.

<u>Limitations of Sample Preparation Procedure</u>

1. Uncured rubber samples should be stored in a freezer (0°C) until they are analyzed.

2. General laboratory precautions concerning the handling and breathing of organic solvents (e.g., THF and ODCB) should be observed.

3. Every precaution should be exercised to protect the dissolved filtered rubber solutions from air and UV light until they are analyzed.

4. Samples should be dissolved, filtered, and analyzed (I.R., G.P.C.) in one working day.

5. Scrupulously clean, lint, and particle free containers must be used for storing the filtered polymer solution. Microscopically small particles may plug the G.P.C. column.

6. The rubber samples do not reproducibly filter. Some losses (up to 50% w/w) of polymer (particularly on the Celite bed) are to be expected.

B. Gel Permeation Chromatography

1. Inject 100-600 μl (depending upon polymer) onto G.P.C. columns using conditions listed in Table Two.

2. As the polymer peak begins to elute from the columns, collect the polymer fraction in a small capped bottle for I.R. analysis. One to three polymer fractions are normally collected in order to have enough material for a satisfactory I.R. spectrum.

3. Once the polymer peak has finished eluting and the recorder pen has returned to the baseline, the recorder may be stopped and the Mp, $\overline{Mw}$, $\overline{Mn}$, and D values calculated as discussed in Section IV-B and Appendix One.

4. Precautions to consider and the limitations of this technique have been described in Section IV-B-4.

C. Infrared Analysis

1. Reduce the volume of the polymer fraction by gently evaporating under a stream of N_2.

2. Quantitatively transfer the reduced volume (3-5 drops) to the AgBr plate. Evaporation of this final volume can be speeded up by gentle heating under a heat lamp and a stream of N_2. (Note: the Wilks AgBr plates have a lip on the outer edge which prevents solvent/polymer from creeping off the AgBr plate).

3. Place AgBr plate in the beam condenser and scan the 2-40 micron range using a slow scanning speed.

4. Before removing the polymer spectra, overlay polystyrene calibration marks.

5. Compare recorded spectra with standard reference spectra.

6. Precautions to consider and the limitations of this technique have been described in Section IV-C-3.

7. Samples of polymers collected by G.P.C. and the I.R. spectrum should be recorded in the same working day.

D. Pyrolysis Gas Chromatography

At this point in the analysis procedure, the general chemical nature of the polymer type should be determined from the I.R. analysis and parameters characteristic of the polymer (Mp, $\overline{M}n$, Mw and D) from the G.P.C. analysis. Should it be necessary to confirm the general chemical nature of the polymer, then a P.G.C. analysis should be run. From the results of this study it appears that little additional complimentary information (complimentary to I.R.) is derived from the P.G.C. analysis. Since the mechanism for identification of the polymer is different by P.G.C. and I.R. P.G.C. could be used if it wer not possible to obtain an I.R. spectrum.

1. Weigh a 50 μg sample of solid uncured rubber sample on an electrobalance (e.g., Cahn Model #4700).

2. Place rubber sample in the silica tube in the pyrolyzer probe.

3. Using the optimized G.C. and pyrolysis conditions given in Table One, pyrolyze the sample and record the pyrogram.

4. To identify the polymer type, compare the sequencing and retention times of the peaks for the unknown polymers with those in standard, reference polymer pyrograms. Standard reference pyrograms can be generated by pyrolyzing the polymer fraction from the G.P.C. analysis of known rubber samples using optimized conditions listed in Table One.

5. Precautions to consider and the limitations of the technique have been described in Section IV-A.

6. Before proceeding to a pyrolysis of another sample, the silica tube in the pyrolyzer probe must be checked for residue contamination and cleaned should contamination be present.

E. Discussion of Cost Related Factors

1. Initial Equipment and Supplies Investment (estimated costs).

a. P.G.C. (Please refer to Table One for a list of the specific equipment used in this project.)

i.	Gas Chromatograph	$10,000.
ii.	Columns (Two, glass)	200.
iii.	Reporting Integrator/Calculator	8,000.

iv.	Gas Regulators and In-Line Gas Dryers	500.
v.	Expendable Supplies (Recorder paper, He, H_2, Air, Syringes, Misc. Fittings, and Leak Detector)	500.
		$19,200

b. G.P.C. (Please refer to Table Two for a list of the sepcific equipment used in this project)

i.	Liquid Chromatograph	$15,000.
ii.	Columns (One "Bank" of Five)	2,500.
iii.	Dual Pen Recorder	2,500.
iv.	Expendable Supplies (Recorder Paper, Solvents, Syringes, Solvent Clarification Kit and Filters, Misc. Fittings)	1,000.
		$21,000.

c. I.R. (Please refer to Section IV-D for specific equipment used in this project).

i.	I.R. Spectrophotometer (2-40μ)	$16,000.
ii.	4x Beam Condenser	1,500.
iii.	Expendable Supplies (Chart Paper, AgBr plates, Syringes, Solvents)	250.
		$17,750.

2. Time, Cost, Manpower Analysis

a. Time estimates G.P.C.

i.	Sample preparation (8 samples)	2 hrs.
ii.	Chromatographic runs (30 min. @)	4 hrs.
iii.	Data reduction (w/o computer assistance - 15 min. @)	2 hrs.

b. Time Estimates I.R.

i.	Sample collection (8 samples) (see G.P.C. runs)	--
ii.	Thin Film Preparation (10 min. @)	1 hr. 20 min.
iii.	I.R. analysis (15 min. @)	2 hrs.
iv.	Data reduction (10 @)	1 hr. 20 min.

c. Time Estimates P.G.C.

i.	Sample preparation and weighing (8 samples) (5 min. @)	40 min.
ii.	Pyrograms (40 min @)	5 hr. 20 min.
iii.	Data Reduction (10 min @)	1 hr. 20 min.

d. Manpower Analysis

Because of the natural division among instrumentation, two persons could run the eight samples per day indicated in 2a, 2b, 2c above. The limiting time factor is the time of the G.P.C. separation of the polymer fraction. One person could run G.P.C. and I.R. analyses, and one person could run P.C.G. and/or I.R. analyses. Should it not be necessary to run P.G.C. analyses, one person should be able to run G.P.C. and I.R. analyses of 8 samples per work day (8 hrs.)

e. Cost Analysis

i.	P.G.C.	
	Gases - 3 tanks ($75 @)/2 wks	$ 225.
	Misc. supplies @$50/wk.	100.
		$ 325.
	8 samples/day x 10 days	80 samples
	Est. Cost of Analysis	$4/sample
ii.	G.P.C.	
	Solvents @$80/bottle x 2/wk.	$ 160.
	Sample Filters @ $1/sample x 40/wk.	40.
	Misc. Supplies $50/wk.	50.
		$ 250.
	8 samples/day x 5 days	40.
	Est. Cost of Analysis	$6.25/sample
iii.	I.R.	
	Misc. Costs $1/sample x 40 samples/wk	$ 40.
	8 samples/day x 5 days	40.
	Est. Cost of Analysis	$1.00/sample

This cost analysis does not include initial capital outlay for equipment (Sections E-1a, 1b, 1c), personnel costs, or normal maintenance for an average equipped laboratory.

<u>Summary</u>: For an average equipped chemistry laboratory with the capital equipment indicated (an investment of $58,000), two technicians of average ability should be able to routinely monitor a minimum of 40 samples per week using the total integrated procedure (i.e., G.P.C., P.G.C., and I.R.) at a cost of $450 for expendable items. Should P.G.C. not be needed, the manpower requirement could be decreased by one person and at a cost of $290 for expendable items.

VI. Other Techniques

ASTM has at least two volumes in the curr nt testing series devoted to testing procedures specifically for rubber and rubber products. The following ASTM procedures deal with some phase of the analysis of rubber and rubber products: D297, D1278, D1416, D2006, D2007, D2226, D2702, D2703, and D3156. (Specific titles for the procedures are listed in Appendix Two). Recalling that the redefined goal of this project was the identification, characterization, and monitoring of the polymer fraction in butyl, Neoprene, and natural based uncured, compounded rubber samples, most of these procedures are not applicable to the work of this project.

Only two of the ASTM procedures (D297, D1278) deal (in part) with the chemical analysis of uncured, compounded rubber. Procedures for qualitatively identifying (from combustion products) the polymer type and for quantitatively determining the weight percent of that polymer (by wet chemical oxidation) can be found in D297. Procedures for natural, Neoprene, and butyl based rubber samples can be found in D297.

The ASTM D1278 procedure deals specifically with the characterization of uncured compounded natural rubber. The quantitative weight-percent procedure used in D1278 is essentially the same one used in D297.

The polymer analysis procedures suggested in D297 and D1278 involve classical wet chemical analysis. The information derived from these procedures is useful and in the instance of the presumptive qualitative test for polymer type, may be complimentary to the work conducted in this project. However, neither procedure is capable of producing information which could be used to characterize the performance characteristics of the finished, cured, compounded rubber material. Literature sources indicate that the molecular weight/molecular weight distribution of the polymer in a rubber sample can directly affect the performance characteristics of a finished rubber product. In light of this information, we feel the analytical procedures evaluated in this project are better suited to a quality control program designed to project performance characteristics of finished rubber products. The relationship between the procedures evaluated in this project and those described in ASTM D279 and D1278 is best summarized by quoting a statement made in D297 concerning instrumental techniques, "Quantitative and qualitative analysis of rubber polymers in rubber products is possible by I.R. of polymers and/or pyrolyzates, but is beyond the scope of D297."

ASTM D2702 deals in a general sense, with the use of I.R. for characterizing rubber chemicals; however, no reference to specific rubber chemicals is given.

VII. Future of Work Direction

A. Goal of Present Project

1. Telephone conversations with the manufacturer of the pyrolyzer (Dr. E Levy of Chemical Data Systems) indicate that is may be possible, using a rubbon probe and solutions of polymers, to differentiate polymers of the same general chemical type (e.g., Neoprene from Neoprene W). This new information should be evaluated in light of the goal of this project and the conclusions of the present study which suggest otherwise.

2. Every attempt should be made to establish the validity of the molecular weight parameters (Mp, $\bar{M}w$, $\bar{M}n$ and D) determined in this study. Contact with polymer scientists both in the polymer industry and the G.P.C. industry should be made in this respect. Additional sets of specification and off-specification polymer samples should be analyzed to provide a larger statistical base for the data. Manufacturer and/or performance standards should not be considered until this statistical data base has been established.

B. Goal of Future Work

1. The antidegradent/curing agent/additive package in uncured compounded butyl, Neoprene, nitrile and natural rubber samples should be analyzed by G.P.C., I.R. and P.G.C. These analysis methods should be evaluated for their ability to monitor the components of the antidegradent/curing agent package aspect of a quality control program.

   The goal of this future work should be an integrated procedure which is compatible with and complimentary to the integrated procedure for the polymer characterization proposed in this project.

2. Several sets of specification and off-specification uncured, compounded rubber samples (in terms of both polymer and additives) should be prepared and analyzed as a test of the integrated (I.R., G.P.C., P.G.C.) procedure for both polymer and additives.

3. The same specification and off-specification uncured compounded rubber samples (#2 above) should be cured and subject to approrpiate wear testing in order to evaluate in a "cause-to-effect" relationship the variations in polymer and additive composition in uncured compounded rubber samples. A computer assisted data analysis program should be used to assist in this phase of the proposed future work.

VIII. Annotated Bibliography

1. Cazes, J., *J. Chem. Ed.*, 43, A567 & A625, 1966.

2. Cazes, J., Gel Permeation Chromatography, American Chemical Society, Washington, D.C., 1971.

3. Adams, H.E., et al., *J. Appl. Polym. Sci.*, 17, 269, 1973.

References 1-3 provide a basic review of theory and application of G.P.C. Specific steps for making $\overline{M}w$, $\overline{M}n$ and D calculations are given in these references.

4. Gaylor, V.F. and James, H.L., *Anal. Chem.*, 50, 29R, 1978.

5. Abbott, S.D., *Amer. Lab.*, 9, 41, 1977.

6. Ouano, A.C., et al., *J. Polym. Sci.*, 12, 307, 1974.

7. Swanson, C.L., *J. Appl. Polym. Sci.*, 18, 1549, 1974.

References 4-7 discuss a variety of sample handling and instrumental problems which the analyst should be aware of when running G.P.C. analyses.

8. ASTM Procedure D3536-76.

Reference 8 provides a step-by-step procedure for performing a G.P.C. calibration run using polystyrene standards. Many helpful hints are given in Reference 8.

9. Dr. Eugene Ley, Personal Communication with respect to ASTM 3-19 Committee's Fourth Correlation Trail for P.G.C.

Reference 9 (E-19 Correlation Trial) provides a standardization procedure which is aimed at improving the reproducibility inter-laboratory P.G.C. data.

Appendix One

Sample Calculation of Mw, Mn, and D
(Typical Data)

Elution Volume,* ml/cm	Height, H* (mm)	Molecular Weight**	Col 2/Col 3	Col 2 x Col 3
20.1	2.5	2,400,000	0.------	6,000,000
20.6	10.0	1,400,000	0.00001	14,000,000
21.1	21.5	840,000	0.00003	18,060,000
21.6	41.5	490,000	0.00008	20,335,000
22.1	62.0	290,000	0.00021	17,980,000
22.6	79.0	190,000	0.00042	15,010,000
23.1	85.5	135,000	0.00063	11,542,500
23.6	82.5	100,000	0.00083	8,250,000
24.1	72.0	74,000	0.00097	5,328,000
24.6	57.0	52,000	0.00110	2,964,000
25.1	43.0	38,000	0.00113	1,634,000
25.6	33.0	27,000	0.00122	891,000
26.1	25.0	19,000	0.00132	475,000
2616	18.5	14,000	0.00132	259,000
27.1	15.0	10,000	0.00150	150,000
27.6	11.0	7,000	0.00157	77,000
28.1	8.0	5,200	0.00154	41,600
28.6	3.0	3,700	0.00081	11,100
Totals	670.0		0.01469	120,007,700

*Data from accompanying recorder trace.

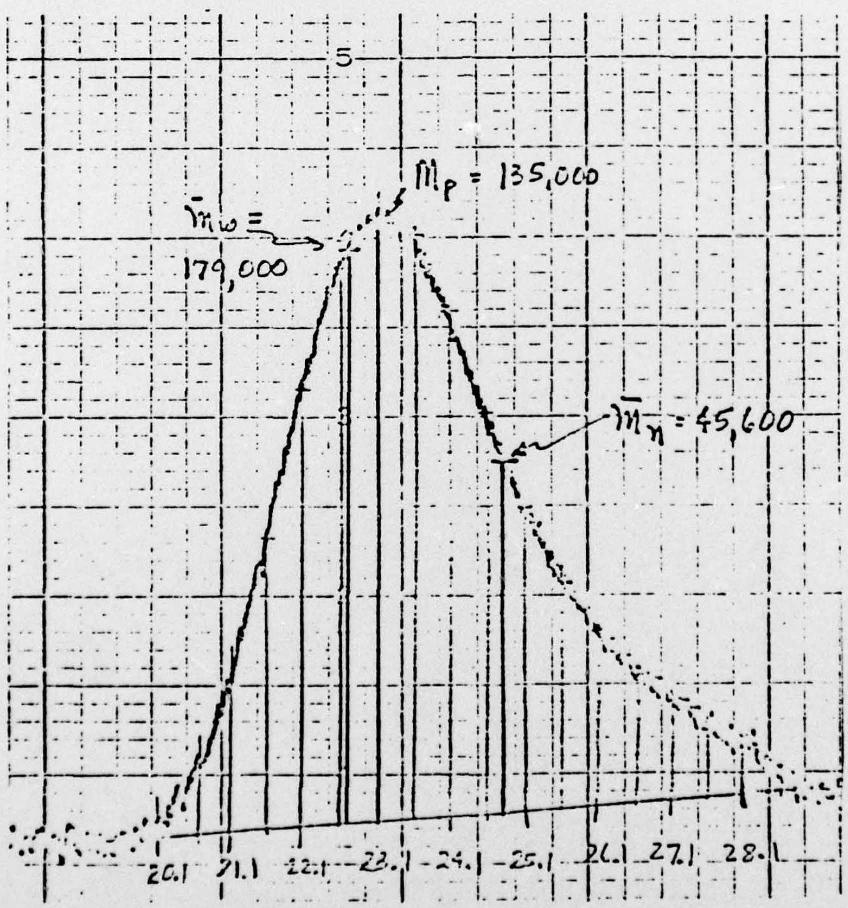
**Data from polystyrene calibration curve.

Appendix One (Cont.)

$$\overline{M}n = \frac{\text{Column 1}}{\text{Column 2}} = \frac{670}{0.01469} = 45,600$$

$$\overline{M}w = \frac{\text{Column 5}}{\text{Column 1}} = \frac{120,000,000}{670} = 179,000$$

$$D = \frac{\overline{M}w}{\overline{M}n} = 3.93$$



Typical Reocrder Trace for G.P.C. Chromatogram. Data in Table taken from this trace.

Appendix One (Cont.)

Specific details for calculating $\overline{M}w$, $\overline{M}n$ and D have been discussed by Cazes (1) and Adams (2). Basically, the parameters $\overline{M}w$, $\overline{M}n$ and D provide a quantitative means of describing the data recorded for each experimental run. As such, they describe the "shape" of the curve and thus provide a means of comparing data. G.P.C. in conjunction with molecular weight parameters has been used to monitor such parameters as the variation in molecular weight of a polymer during a production run and variation in polymer, dye, colorant, antioxidant, and plasticizer as they relate to a "good" or "bad" finished polymer products (3-7). The use of G.P.C. to monitor the polymer in uncured, compounded rubber samples should be a natural application (as suggested in this project) once sufficient data has been generated and analyzed.

Appendix Two

Titles of Selected ASTM Procedures Dealing with the Analysis of Rubber and Rubber Containing Materials

ASTM #	Title
D297	Chemical Analysis of Rubber Products
D1278	Chemical Analysis of Natural Rubber
D1416	Chemical Analysis of Synthetic Elastomers
D2006	Tests for Characteristic Groups in Rubber Extender and Processing Oils by the Precipitation Method
D2007	Tests for Characteristic Groups in Rubber Extender and Processing Oils by the Clay-Gel Adsorption Chromatographic Method
D2226	Recommended Practice for Description of Types of Petroleum Extender Oils
D2663	Tests for Degree of Dispersion of Carbon Black in Rubber Compounds
D2702	Recommended Practice for Determination of I.R. Characteristics of Rubber Chemicals
D2703	Recommended Practice for Determination of UV Absorption Characteristics of Rubber Chemicals
D3156	Recommended Practice for TLC Analysis of Antidegradents (Stabilizers, Antioxidants, and Antiozonants) in Raw and Vulcanized Rubbers